Investigation on Effective Parameters onto Graft Copolymerization Pectin with Methacrylamide

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In this work, large numbers of carboxamide functional groups were introduced onto pectin by grafting with polymethacrylamide (PMAAm). The effects of various reaction conditions such as monomer, polysaccharide, initiator concentration and reaction temperature on the percentage of add-on %, graft yield (G %) and graft efficiency (GE %) were investigated.

Key Words: Pectin, Methacrylamide, Grafting parameters, Modify structure.

INTRODUCTION

Pectin is a naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry. It has been used successfully for many years in the food and beverage industry as a thickening agent, a gelling agent and a colloidal stabilizer. Pectin also has several unique properties that have enabled it to be used as a matrix for the entrapment and/or delivery of a variety of drugs, proteins and cells. However, it may need to be further modified for some special applications[1-3].

Among the diverse approaches that are possible for modifying polysaccharides, grafting of synthetic polymer is a convenient method to add new properties to a polysaccharide with minimum loss of the initial properties of the substrate[2]. Graft copolymerization of vinyl monomers onto polysaccharides using free radical initiation has attracted the interest of many scientists. Up to now, considerable works have been devoted to the grafting of vinyl monomers onto the substrates, specially cellulose[3]. Of the monomers grafted, acrylonitrile (AN) has been the most frequently used one, mainly due to its highest grafting efficiency[2,4], improving the thermal resistance of the graft copolymer[5] and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents[2,5].

The literature survey, reveals that few of the modifications deal with chemical grafting of a pre-modified polysaccharide such as pectin. Ammonium persulfate-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate[5,6], AN/methyl methacrylate mixture[7] and 4-vinylpyridine[8,9], onto pectin has been reported. However, to the best of our knowledge, no report has been published on the optimization of AAm graft polymerization onto pectin using APS-saccharide initiating system. As a part of our research program on polysaccharide modification, herewith we report the optimized APS-induced synthesis of PE-g-polymethacrylamide under an inert atmosphere.

EXPERIMENTAL

Synthesis of copolymer: A facial one step preparative method was used for synthesis of Pec-polymethacrylamide copolymer. Pectin (0.50-1.5 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of pectin to form a homogeneous solution, a definite amount of ammonium persulfate solution (0.15 g in 5 mL H_2O) was added to pectin solution and was allowed to stir for 10 min. After adding ammonium persulfate, certain amounts of monomer (MAAm 1.50 g in 5 mL H_2O) was added to the pectin solution. After 90 min, the reaction product was allowed to cool to ambient temperature. The produced material was poured to excess non solvent ethanol (200 mL) and kept for 3 h to remove water. Then ethanol was decanted and the product scissored to small pieces. Finally, the filtered copolymer is dried in oven at 60 ºC for 10 h.

Homopolymer extraction: The graft copolymer, namely pectin-g-polymethacrylamide, was freed from poly methacrylamide homopolymer, by pouring 0.50 g of the product in 50 mL of dimethylformamide (DMF) solution. The mixture was stirred gently at room temperature for 48 h. After complete removal of the homopolymer by centrifugating , the pectin-g-polymethacrylamide was filtered, washed with methanol and dried in oven at 50 ºC to reach a constant weight[10].

RESULTS AND DISCUSSION

Characteristic and determination of important-grafting parameters: The percentage of conversion (PC %), graft yield (Gr %) and graft efficiency (GE %) were evaluated with the following weight-basis expressions as reported by Fanta and Doane[11]:

From the increased weight, the percentage conversion (PC %) can be estimated as the following equation:

$$PC\ (\%) = 100\frac{(W_2 - W_0)}{W_1} \quad (1)$$

where W_0, W_1 and W_2 designate the weight of pure pectin substrate, MAAm monomer in feed and total weight product (copolymer and homopolymer), respectively. In this study, the value of W_1 was fixed at 0.75 g. The rough products were extracted by dimethylformamide solution in a centrifugating apparatus at least 48 h for the complete removal of the homopolymer. The graft yield (Gr %) and graft efficiency (GE %) are estimated as follows[12]:

$$Gr\ (\%) = 100\frac{(W_3 - W_0)}{W_0} \quad (2)$$

$$GE\ (\%) = 100\frac{(W_3 - W_0)}{(W_2 - W_0)} \quad (3)$$

or

$$GE\ (\%) = \frac{100(W_3 - W_0)}{(W_4 + W_3 - W_0)}$$

$$Hp\ (\%) = \frac{W_4}{(W_3 + W_4)} \quad (4)$$

$$Add\text{-}on\ (\%) = \frac{(W_e - W_0)}{W_3} \quad (5)$$

where W_3 and W_4 are the dried weight of grafted pectin after extraction and polymethacrylamide homopolymer.

Optimization of the reaction conditions: In the present investigation, the effect of concentration of APS and MAAm, pectin along with reaction time and temperature was studied, to optimize the reaction conditions. It may be found from the related curves (next figures) that the trends of the "changes" are similar for grafting parameters graft yield, graft efficiency and Add-on. The reason is the similar concepts applied for defining the grafting parameters (eqns. 1-5).

Effect of initiator concentration: The grafting dependence on APS concentration can be concluded from Table-1. As showed in Fig. 1, the highest grafting ratio (455 %) was achieved at 0.05 mol/L of APS where homopolymer content was 6.6 %. Increased initiator concentration resulted in more radical sites on the polysaccharide backbone that in turn led to higher grafting and add-on values and lower homopolymer formation. However, the number of active free radicals on the pectin backbone is increased in terms of the initiator levels lower than 0.05 mol/L. This accounts for the initial increment in grafting ratio up to a certain amount of APS. The grafting ratio decrease after the maximum may be attributed to increased number of produced radicals led to terminating step *via* bimolecular collision resulting in enhanced crosslink density[10].

TABLE-1
GRAFTING PARAMETERS FROM THE GRAFT
POLYMERIZATION OF METHARCRYLAMIDE ONTO PECTIN
AT DIFFERENT CONCENTRATION OF THE APS

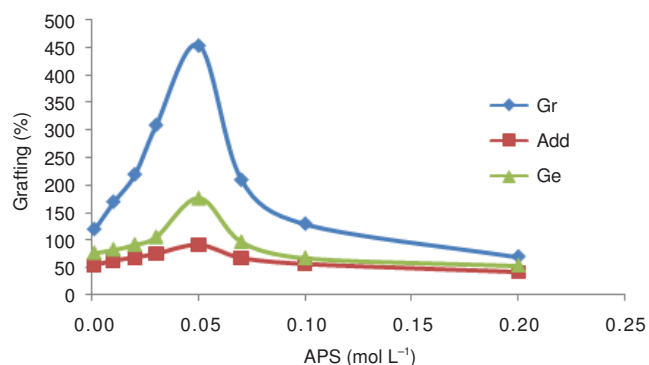| APS (M)	T (°C)	Time (min)	PC (%)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.001	45.00	60.00	63.00	117.00	27.00	70.50	75.50
0.010	45.00	60.00	67.70	163.00	21.40	73.60	77.50
0.020	45.00	60.00	76.00	235.00	11.90	81.80	90.10
0.030	45.00	60.00	81.80	318.00	9.10	84.00	96.80
0.050	45.00	60.00	88.70	455.00	6.60	91.80	93.10
0.070	45.00	60.00	84.00	210.00	12.90	80.20	91.70
0.100	45.00	60.00	65.80	130.00	27.80	77.00	87.00
0.200	45.00	60.00	51.00	70.00	33.40	73.50	82.60

Fig. 1. Effects of initiator concentration on the graft copolymerization. Reaction conditions: pectin 1.2 wt %, MAAm 0.3 M, temp. 45 ºC, time 1 h

Effect of MAAm concentration: The copolymerization of grafting MAAm onto pectin was carried out at different acrylamide concentrations ranging from 0.05-0.5 mol L^{-1} (Table-2). The effect of MAAm concentration on the graft copolymerization is shown in Fig. 2. The increase in GE % is due to the fact that more MAAm monomers are present to react with pectin macroradicals with initially increasing MAAm concentration, but with the further increase of MAAm concentration after a critical value being reached, the homopolymerization probability of methacrylamide increased, usually resulting in the decrease of GE %. G % is a function of GE %, PC % and monomer weight in feed (W_1). From the eqns. (1-3), the relationship between G % and GE %, PC %, W_1 can be deduced as the following equation[13]:

$$G\ (\%) = \frac{100(W_1 \times PC \times GE)}{W_0} \quad (6)$$

TABLE-2
GRAFTING PARAMETERS FROM THE GRAFT
POLYMERIZATION OF METHARCRYLAMIDE ONTO
PECTIN AT DIFFERENT AMOUNT OF THE MONOMER

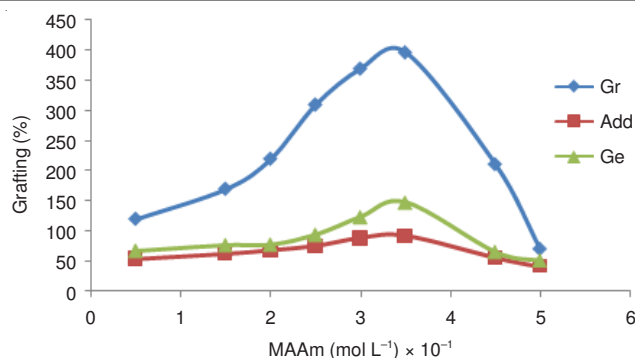| MAAm (M)	T (°C)	Time (min)	PC (%)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.05	45.00	60.00	68.00	120.00	33.40	51.30	67.70
0.15	45.00	60.00	72.50	170.00	25.30	58.90	77.10
0.20	45.00	60.00	77.40	220.00	19.90	66.30	78.00
0.25	45.00	60.00	83.20	310.00	13.60	73.40	94.50
0.30	45.00	60.00	91.00	370.00	9.80	88.70	124.00
0.35	45.00	60.00	94.60	397.00	8.70	92.00	148.00
0.45	45.00	60.00	88.60	211.00	27.20	56.50	71.30
0.50	45.00	60.00	80.50	70.00	26.48	41.70	49.10

Fig. 2.   Effects of MAAm concentration on the graft copolymerization. Reaction conditions: pectin 1.2 wt %, APS 0.05 M, temp. 45 ºC, time 1 h

The decrease of G % and Ge % with further increase in the MAAm concentration may be explained as follows: (a) preferential homopolymerization over graft copolymerization, (b) increasing the viscosity of reaction medium, which hinders the movement of free radicals and (c) increase in the chance of chain transfer to monomer molecules. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose, and methyl acrylate onto starch.

Effect of pectin concentration: The related to the grafting dependence on pectin amount is summarized in Table-3. As shown in Fig. 3, maximum grafting and the lowest homopoly-acrylamide formation was observed at 1.50 wt % pectin, while others reactants including, monomer, initiator and temperature were kept constant. Beyond this value, both grafting ratio and add-on values are considerably reduced. This behaviour is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (from 0.20-1.50 wt % pectin). However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of macroradicals leading to decreased grafting ratio and add-on values[14]. It may also be attributed to deactivation of the macroradical growing chains (*e.g.*, by transfer reactions, combination and/or interaction with the primary radicals) soon after their formation[10].

TABLE-3
GRAFTING PARAMETERS FROM THE GRAFT
POLYMERIZATION OF METHARCRYLAMIDE ONTO PECTIN
AT DIFFERENT CONCENTRATION OF THE SUBSTRATE

Pec (wt %)	T (ºC)	Time (min)	PC (%)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.20	60.00	60.00	63.70	187.00	33.20	73.70	52.60
0.30	60.00	60.00	66.80	239.00	26.80	78.60	54.10
0.40	60.00	60.00	74.10	365.00	19.00	84.80	75.90
0.50	60.00	60.00	77.30	376.00	14.70	87.30	94.60
1.00	60.00	60.00	87.50	415.00	12.30	92.70	106.00
1.50	60.00	60.00	92.80	477.00	11.00	94.00	166.00
2.00	60.00	60.00	90.60	219.00	17.50	72.10	97.00
2.50	60.00	60.00	86.30	103.00	26.30	55.40	72.70
3.00	60.00	60.00	77.00	55.30	28.30	43.00	61.20

Effect of temperature: To study the influence of the reaction bath temperature on the grafting parameters, the grafting of MAAm onto pectin was carried out at six temperature ranging from 40-75 ºC. The results are given in Table-4. As shown in Fig. 4, grafting percentage (Gr %) is increased
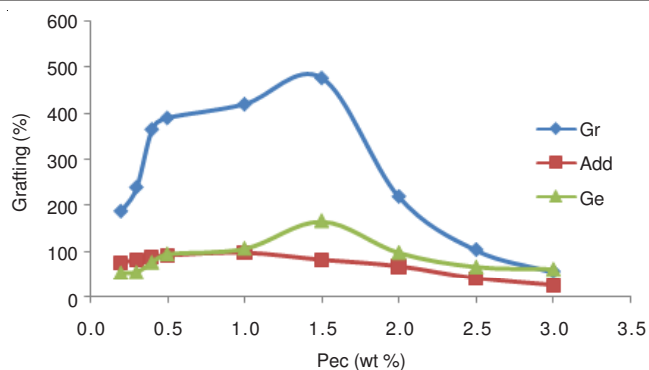

Fig. 3.   Effect per cent weight of pectin on the grafting parameters. Reaction conditions: APS 0.05 M, MAAm 0.35 M, temp. 45 ºC, time 1 h

TABLE-4
GRAFTING PARAMETERS FROM THE GRAFT
POLYMERIZATION OF METHARCRYLAMIDE ONTO
PECTIN AT DIFFERENT TEMPERATURES

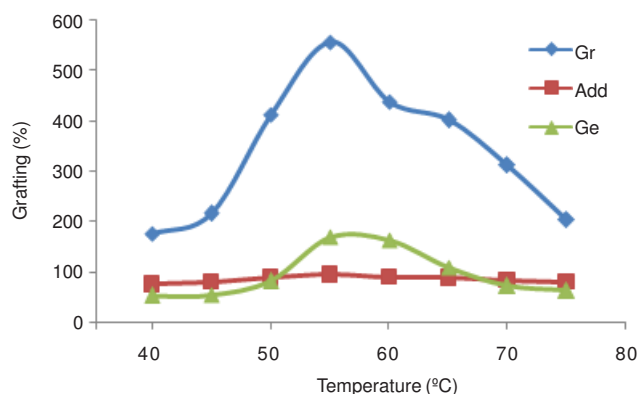| T (ºC)	Time (min)	PC (%)	Gr (%)	Hp (%)	Add (%)	Ge (%)
40.00	60.00	66.66	177.00	37.10	75.70	66.22
45.00	60.00	72.70	216.00	22.60	80.40	94.10
50.00	60.00	84.80	413.00	17.60	88.00	122.30
55.00	60.00	95.70	557.00	12.00	95.10	170.00
60.00	60.00	90.20	438.00	13.40	88.50	164.20
65.00	60.00	87.30	402.00	19.00	83.80	109.00

Fig. 4.   Effects of reaction temperature on the graft copolymerization. Reaction conditions: pectin 1.5 wt %, APS 0.05 M, MAAm 0.35 M, time 1 h

with increasing the temperature from 40-55 ºC and then decreased. At 55 ºC, maximum grafting (Gr 557 %), minimum homopolymer content (12 %) and highest add-on value (95.3 %) was obtained. Improvement of grafting up to 55 ºC can be attributed to the following factors: increased the number of free radicals formed on the pectin backbone, increased propagation of the graft copolymerization onto pectin, enhanced diffusion of monomer and initiator into and onto backbone structure and increased in mobility of the monomer molecules and their higher collision probability with the backbone macroradicals[15,16]. However, graft yield was decreased as the bath temperature was raised beyond 55 ºC. This can be accounted for in terms of chain radical termination at higher temperatures. Premature termination of growing chains and instability of the APS-saccharide complex are presumably another reasons for reduced amount of grafting beyond 55 ºC. The homopolymer formation is minimal at the bath temperature of 55 ºC[17].

Conclusion

A novel copolymer, Pec-g-polymethacrylamide, was synthesized in an aqueous solution by graft copolymerization of methacrylamide monomer onto pectin backbone using ammonium persulfate as an initiator in water solution. The main factors affecting the grafting parameters, including concentration of the initiator, monomer and pectin, reaction time and both temperature was studied in detail. The optimum reaction conditions were found to be ammonium persulfate 0.05 mol/L, MAAm 0.35 mol/L, pectin 1.50 % wt, reaction temperature 55 ℃ and time reaction 1 h. Under the optimized conditions the grafting parameters were calculated to be grafting yield % 557, graft efficiency % 170, percentage of conversion % 95.7 , HP % 12 and add-on % 95.10 %.

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